

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Registered in U. S. Patent Office. © Copyright, 1970, by the American Chemical Society

VOLUME 92, NUMBER 12

JUNE 17, 1970

Physical and Inorganic Chemistry

Chemistry without Spin¹

F. A. Matsen

Contribution from the Molecular Physics Group,
The University of Texas at Austin, Austin, Texas. Received January 21, 1970

Abstract: The coarse structure of chemistry is that part of chemistry which does not include fine structure, hyperfine structure, and magnetic effects. Coarse structure chemistry embraces the major portion of conventional chemistry, *e.g.*, molecular geometry and chemical reactivity. Coarse structure phenomena are predicted by a spin-free-Hamiltonian operating on a spin-free vector space. The spin-free N -electron Hamiltonian commutes with S_N , the group of permutations on the spin-free coordinates. The spin-free coarse structure states are labeled by the Pauli-allowed partitions, $[\lambda] = [2^p, 1^{N-2p}]$, where p is an integer that ranges from 0 to $N/2$. A widely used, but theoretically irrelevant, labeling of spin-free, coarse structure states is by the spin quantum number, $S \equiv N/2 - p$. Outside of coarse structure chemistry, $[\lambda]$ (and in consequence, S) is a poor quantum number. It follows that in all chemical problems spin is either a theoretically irrelevant quantum number or a poor one. Many chemists believe that spin plays an energy-determining role in coarse structure chemistry. This has led to a number of widely held misconceptions about spin. These misconceptions are itemized and analyzed in detail.

1. Introduction

The aim of this paper is to point out that spin plays only a very minor role in most of chemistry. The belief that spin plays a major role has led to a number

Table 1.1. Popular Misconceptions about Spin

- (1) Chemical bonding is due to spin energetics
- (2) Repulsion occurs between nonbonded atoms because electrons with parallel spins repel
- (3) The energy separation between singlet and triplet states is due to spin energetics
- (4) The existence of high- and low-spin states in transition metal complexes is due to spin energetics
- (5) Paramagnetic susceptibilities are determined by spin energetics
- (6) Spin densities are determined by spin energetics
- (7) Spin is the analog of classical angular momentum, and since classical angular momentum is conserved, spin must be conserved in chemical reactions
- (8) The mechanisms of many reactions are determined by spin energetics
- (9) In the course of the reaction, singlet \rightleftharpoons triplet, an instantaneous spin-flip occurs
- (10) Electric dipole transitions between different spin states are forbidden because spin does not interact with an electric field

(1) Supported by the Robert A. Welch Foundation of Houston, Texas.

of misconceptions, some of which are listed in Table 1.1. In this section an assessment of the role played by spin is carried out in three steps: (1) a brief description of the spin formulation of quantum chemistry, (2) a brief description of the spin-free formulation, and (3) an analysis of possible sources of the misconceptions in Table 1.1.

Chemistry can be subdivided into three subchemistries according to the type of effective Hamiltonian, \mathbf{H}_{eff} , required to make meaningful predictions: (a) coarse structure chemistry

$$\mathbf{H}_{\text{eff}} = \mathbf{H}^{\text{SF}} = \sum_i \mathbf{H}_i^{\text{SF}} + \sum_{i < j} \frac{e^2}{r_{ij}} \quad (1.1)$$

(the superscript SF means spin-free); (b) fine structure chemistry

$$\mathbf{H}_{\text{eff}} = \mathbf{H}^{\text{SF}} + \text{electron spin terms} \quad (1.2)$$

and (c) hyperfine structure chemistry

$$\mathbf{H}_{\text{eff}} = \mathbf{H}^{\text{SF}} + \text{electron and nuclear spin terms} \quad (1.3)$$

Coarse structure chemistry comprises a very large part of all of chemistry, embracing quantities such as

molecular reactivity and geometry. The following facts concerning coarse structure chemistry are well known.

(A.1) There exists a spin formulation of coarse structure chemistry which employs spin operators, spin functions, and the antisymmetry principle.

(A.2) Coarse structure states are labeled by the spin quantum number, S , which is determined by the total spin operator \mathbf{S}^2 acting on an antisymmetric eigenfunction. A coarse structure state may also be labeled by an array of arrows such that

$$S = |n(\uparrow) - n(\downarrow)|/2$$

where $n(\uparrow)$ and $n(\downarrow)$ are the numbers of electrons whose spin is pointed up and down, respectively. Coarse states may also be labeled by the multiplicity

$$2\mathfrak{N} = 2S + 1 \quad (1.4)$$

The following facts concerning coarse structure chemistry are not well known.

(B.1) There exists a spin-free formulation of coarse structure chemistry based on the commutation of the spin-free Hamiltonian (eq 1.1) with the group (the symmetric group, S_N) of permutations on the spin-free coordinates of the N electrons.

(B.2) Coarse structure states are labeled by the irreducible representations of S_N . These are the partitions $[\lambda]$ of N and are called *permutation quantum numbers*. For electrons, the Pauli-allowed partitions, called *spin-free quantum numbers*, are

$$[\lambda] = [2^p, 1^{N-2p}] \quad (1.5)$$

where p is an integer ranging from 0 to $N/2$.

(B.3) As a consequence of (B.1), the conventional spin formulation is not essential. It is, in fact, merely a device for introducing permutational symmetry into the coarse structure problem without recourse to formal group theory.

(B.4) As a consequence of (B.1), (B.2), and (B.3), the spin labeling of the coarse structure states is irrelevant. If a spin labeling is desired, it can be accomplished by the relation

$$S = N/2 - p \quad (1.6)$$

The multiplicity labeling is then

$$2\mathfrak{N} = 2S + 1 = N - 2p + 1 \quad (1.7)$$

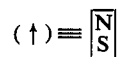
(B.5) Outside of coarse structure chemistry the effective Hamiltonian does not commute with the elements of S_N . Consequently, the spin-free quantum number, $[\lambda]$, is not a good quantum number (see section 7). It then follows from (B.4) that spin is not a good quantum number either.

(B.6) As a consequence of both (B.2) and (B.5), spin is either an irrelevant quantum number or a poor one.

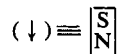
Because of lack of knowledge of items B.1–B.6, many chemists hold misconceptions about spin (see Table 1.1). These misconceptions appear to be based on the following incorrect axioms.

A. Spin Energetics Axiom

An electron with spin is an elementary magnet which may take one of two orientations in space

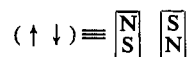


and

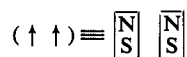


The important energy term for two electrons is the classical energy of the two elementary magnets. From this axiom the following predictions are made.

(1) The singlet state



lies lower in energy than does the triplet state



(2) Nonbonded atoms repel at small separations because of the presence of electrons with parallel spin.

(3) The chemical bond in the ground (singlet) state of H_2 is a magnetic one represented by



(4) Electrons can spin polarize each other affecting spin densities and hyperfine structure.

Comments. Singlet–triplet separation (see section 3), nonbonded repulsion (see section 4), chemical bonding (see section 5), and spin densities (see section 8) are predicted by a spin-free Hamiltonian and are independent of spin energetics. A possible source of the spin energetics axiom is the use of the classical magnetic dipole–magnetic dipole interaction

$$\varepsilon = k \frac{\vec{\mu}_A \cdot \vec{\mu}_B}{r^3}$$

to set up the Heisenberg effective spin Hamiltonian

$$\mathbf{H} = -2J \vec{S}_A \cdot \vec{S}_B$$

which operates on the spin part of an antisymmetrized function.

B. The Spin Conservative Axiom

Spin is analogous to classical angular momentum and since classical angular momentum is conserved, spin must be conserved also and must be a good quantum number.

Comment. For coarse structure chemistry, the effective Hamiltonian is spin free. Both the spin-free quantum number, $[\lambda]$ (B.2), and the spin quantum number, S (B.4), are good quantum numbers and are conserved (see section 6). Outside of coarse structure chemistry the effective Hamiltonian is not spin free; neither $[\lambda]$ nor S is a good quantum number and they are not conserved (see section 7). The analog of the Wigner spin-conservation rule exists in the spin-free formulation (see section 6). The analogy to classical angular momentum is irrelevant and leads to incorrect predictions.

C. The Spin-Flip Axiom

The spin-flip axiom is a corollary of axiom A. Since spin states are described by arrays of arrows, it follows that in any adiabatic process in which spin is not conserved (called an *intersystem crossover*) arrows must

change their relative orientation. Since each arrow may take only one of two directions, it follows that any rearrangement of arrow orientation must be instantaneous; *i.e.*, the spin must flip. This is often thought to correspond to some sort of quantum jump and to require the instantaneous input or output of energy.

Comments. During an intersystem crossover, spin is a poor quantum number and the system cannot be described by spin arrows, and, in consequence, the crossover process cannot be described by the instantaneous flipping of spin arrows. A correct description of the process is given in section 7.

D. The Spin-Mechanism Axiom

The spin-mechanism axiom states that the mechanism of a number of chemical reactions is determined by spin considerations. For example, a system in a singlet state, since its spins are paired, must react by a concerted mechanism, while a system in a triplet state in which the spins are unpaired can react by a two-step process. A frequently cited example is the retention or loss of geometrical configuration by butene-2 on the addition of singlet or triplet methylene.

Comment. The reaction mechanisms of chemistry are determined in the main by the potential surface predicted by spin-free Hamiltonians. States with different permutational symmetry may or may not have grossly different potential surfaces. Consequently, systems in different spin states may or may not react by the same mechanism. If the different spin states do react differently it is often possible to adduce spin-free rules for the mechanism.² There exists at present for most reactions no concrete evidence for support of the spin-mechanism axiom.

A biradical³ is an intermediate with two free-radical functions. Discussions of biradicals have often been obscured by the misconceptions of the type discussed above. The mechanism by which a biradical reacts is, in general, determined by the spin-free Hamiltonian of the system. The states of the biradical may be characterized in two limiting cases as follows.

(a) If the two free-radical functions are noninteracting, then the resultant singlet and triplet states are completely degenerate, and the distinction between singlet and triplet states is meaningless. The magnetic susceptibility is that of two isolated doublets.

(b) If the two free-radical states are strongly interacting, then the singlet and triplet states are well separated, intersystem crossover is slow, and the system exists either in an essentially pure singlet state and is diamagnetic or in an essentially pure triplet state and is paramagnetic.

The remainder of this paper is concerned with the spin-free formulation of quantum chemistry. The advantage of the spin-free formulation can be summarized as follows.

(1) The spin-free formulation puts permutational symmetry on the same basis as other symmetries, *e.g.*, point group symmetries. This shows that the coarse structure state labeling is group theoretical and does

not depend on the concept of spin nor on the concept of angular momentum.

(2) The spin-free formulation emphasizes the fact that spin plays no energy-determining role in coarse structure chemistry and that the coarse structure dynamics are indeed spin free.

(3) The spin-free formulation is as easy to teach as is the conventional one, if the theory of the symmetric group is included in the conventional group theory course.

(4) The spin-free formulation permits the use of powerful group theoretical theorems whose existence is not obvious in the conventional formulation.

As a consequence of items 1 and 2, the spin-free formulation prevents misconceptions of the type listed in Table 1.1.

The origins of spin-free quantum chemistry are as old as the origin of quantum mechanics itself. In the beginning, Heitler, Weyl, Hund, Wigner, and others applied the theory of the symmetric group to the *N*-electron problem.⁴ However, shortly afterward the introduction of the Slater determinant⁵ practically drove the (symmetric) Gruppenpest out of quantum chemistry. In recent years the (symmetric) Gruppenpest has returned as witnessed by a rather extensive literature. This literature can be divided into two main groups, one which emphasizes the spin-free formulation,⁶⁻²² and one which uses the symmetric group in the conventional spin formulation²³⁻³² of the coarse structure problem.

(4) H. Weyl, "Group Theory and Quantum Mechanics," a reprint of an English translation, Dover Publications, New York, N. Y. (the original German edition is dated 1928).

(5) J. C. Slater, *Phys. Rev.*, **38**, 1109 (1931).

(6) A series of papers under the title Spin-Free Quantum Chemistry: (a) paper I, F. A. Matsen, *Advan. Quantum Chem.*, **1**, 59 (1964); (b) paper II, F. A. Matsen, *J. Phys. Chem.*, **68**, 3282 (1964); (c) paper III, F. A. Matsen, A. A. Cantu, and R. D. Poshusta, *ibid.*, **70**, 1558 (1966); (d) paper IV, F. A. Matsen, *ibid.*, **70**, 1568 (1966); (e) paper V, F. A. Matsen and A. A. Cantu, *ibid.*, **72**, 21 (1968); (f) paper VI, F. A. Matsen and D. J. Klein, *ibid.*, **73**, 2477 (1969); (g) paper VII, F. A. Matsen and A. A. Cantu, *ibid.*, **73**, 2488 (1969); (h) paper VIII, F. A. Matsen and M. L. Elizey, *ibid.*, **73**, 2495 (1969); (i) paper IX, F. A. Matsen and D. J. Klein, "The Aggregate Theory of Polyelectronic Systems," manuscript submitted for publication; (j) paper X, F. A. Matsen and D. J. Klein, *J. Phys. Chem.*, submitted for publication.

(7) I. G. Kaplan, *Zh. Eksp. Teor. Fiz.*, **41**, 460, 790 (1961); *Teor. Eksp. Khim.*, **1**, 608, 619 (1965).

(8) R. D. Poshusta and F. A. Matsen, *J. Math. Phys.*, **7**, 711 (1966).

(9) J. C. Hempel, J. C. Browne, and F. A. Matsen, *J. Mol. Spectrosc.*, **19**, 73 (1966).

(10) G. A. Gallup, *J. Chem. Phys.*, **48**, 1752 (1968); **50**, 1206, 1214 (1969).

(11) R. D. Poshusta and R. W. Kramling, *Phys. Rev.*, **167**, 139 (1968).

(12) G. Heldman, *Int. J. Quantum Chem.*, **2**, 785 (1968).

(13) R. D. Poshusta and F. A. Matsen, "The *N*-representability Problem," Queen's Papers on Pure and Applied Mathematics, No. 11, Kingston, 1968.

(14) J. C. Hempel and F. A. Matsen, *J. Phys. Chem.*, in press.

(15) G. Heldmann and P. Schnupp, *J. Comput. Phys.*, **3**, 208 (1968).

(16) O. Goscinski and Y. Ohrne, *Int. J. Quantum Chem.*, **2**, 845 (1968).

(17) R. C. Morrison and G. A. Gallup, *J. Chem. Phys.*, **50**, 1214 (1969).

(18) (a) D. J. Klein, *J. Chem. Phys.*, **50**, 5140 (1969); (b) *ibid.*, **50**, 5151 (1969).

(19) A. A. Cantu, *Mol. Phys.*, in press.

(20) A. A. Cantu, *ibid.*, in press.

(21) D. J. Klein and R. W. Kramling, *Int. J. Quantum Chem.*, in press.

(22) A. T. Amos and J. I. Musher, *Chem. Phys. Lett.*, **3**, 721 (1969).

(23) R. Serber, *Phys. Rev.*, **45**, 461 (1934); *J. Chem. Phys.*, **2**, 697 (1934).

(24) T. Yamanouchi, *Proc. Phys. Math. Soc. Jap.*, **20**, 547 (1938).

(25) M. Kotani, A. Amemiya, E. Ishiguro, and T. Kimura, "Table of Molecular Integrals," Maruzen, Tokyo, 1955.

(26) M. Kotani, "Colloque sur le Calcul des Fonctions d'onde Moleculaire," CNRS, Paris, 1958.

(2) F. A. Matsen, *J. Amer. Chem. Soc.*, in press.

(3) S. P. McGlynn, T. Azumi, and M. Kinoshita, "The Molecular Spectroscopy of the Triplet State," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1969.

Table 2.1. Permutation and Spin Quantum Numbers for $N = 2, 3,$ and 4

	$[\lambda]$	YD $[\lambda]$	p	S	Arrow representation	\mathfrak{N}	Multiplicity notation
$N = 1$	[1]		0	$1/2$	\uparrow	2	Doublet [D]
$N = 2$	[1 ²] = [1,1]		0	1	$\uparrow \uparrow$	3	Triplet [T]
	[2]		1	0	$\uparrow \downarrow$	1	Singlet [S]
$N = 3$	[1 ³] = [1,1,1]		0	$3/2$	$\uparrow \uparrow \uparrow$	4	Quartet [Q]
	[2,1]		1	$1/2$	$\uparrow \uparrow \downarrow$	2	Doublet [D]
	[3]				\leftarrow Excluded \rightarrow		
$N = 4$	[1 ⁴] = [1,1,1,1]		0	2	$\uparrow \uparrow \uparrow \uparrow$	5	Quintet [Qi]
	[2,1 ²] = [2,1,1]		1	1	$\uparrow \uparrow \uparrow \downarrow$	3	Triplet [T]
	[2] = [2,2]		2	0	$\uparrow \uparrow \downarrow \downarrow$	1	Singlet [S]
	[3,1]				\leftarrow Excluded \rightarrow		
	[4]				\leftarrow Excluded \rightarrow		

2. Spin-Free Quantum Chemistry³³

The spin-free Hamiltonian (eq 1.1) commutes with the permutations of the spin-free coordinates of the N electrons; *i.e.*

$$[\mathbf{H}^{\text{SF}}, \mathbf{P}_a^{\text{SF}}] = 0, \quad \mathbf{P}_a^{\text{SF}} \in S_N \quad (2.1)$$

where S_N is the symmetric group, the group of permutations. It follows from the Wigner-Eckart theorem (eq 2.16) that the irreducible representations of S_N supply exact quantum numbers for \mathbf{H}^{SF} . The irreducible representations of S_N are identified by partitions $[\lambda]$ of N where

$$[\lambda] \equiv [\lambda^1, \lambda^2, \dots], \quad \lambda^1 \geq \lambda^2 \geq \dots \geq 0 \quad (2.2)$$

is a set of integers such that

$$\sum_i \lambda^i = N \quad (2.3)$$

A partition $[\lambda]$ is graphically represented by a Young diagram, YD $[\lambda]$, composed of rows of squares with λ^i squares in the i th row. A condensed form of (2.2) is

$$[\lambda] \equiv [\dots g^{\lambda_g}, \dots, 2^{\lambda_2}, 1^{\lambda_1}] \quad (2.4)$$

where λ_g is the number of integers equal to g in (2.3) such that

$$\sum_g g\lambda_g = N \quad (2.5)$$

See Table 2.1.

(27) M. Kotani in "Handbuch der Physik," Vol. 37, S. Flugge, Ed., Springer Verlag, Berlin-Wilmersdorf, 1961, Part II.

(28) G. F. Koster, Technical Report of the Solid State and Molecular Theory Group, MIT, Cambridge, Mass., 1956.

(29) W. T. Simpson, "Theories of Electrons in Molecules," Prentice-Hall, Englewood Cliffs, N. J., 1962.

(30) W. A. Goodard, *Phys. Rev.*, **157**, 73, 81, 93 (1967); *J. Chem. Phys.*, **48**, 1008 (1968).

(31) F. E. Harris, *Advan. Quantum Chem.*, **3**, 61 (1967).

(32) J. J. Sullivan, *J. Math. Phys.*, **9**, 1369 (1968).

(33) An elementary treatment of the required mathematical background is contained in F. A. Matsen, *Vector Spaces and Algebras for Chemistry and Physics*, Holt, Rinehart and Winston, Inc., New York, N. Y., 1970.

A partition $[\lambda]$ is called a *permutation quantum number* and the state of the Hamiltonian which it identifies is called a *permutation state*. Of the possible permutation states, the only states which occur in nature are the states for which

$$[\lambda] = [2^p, 1^{N-2p}], \quad 0 \leq p \leq N/2 \quad (2.6)$$

These are called *Pauli-allowed spin-free states*. A Pauli-allowed spin-free state can also be characterized by the *multiplicity quantum number*

$$\mathfrak{N} = N - 2p + 1 \quad (2.7)$$

The states are called singlet, doublet, triplet, etc.; states for $\mathfrak{N} = 1, 2, 3,$ etc. We will often replace $[\lambda]$ by the symbols [S], [D], [T], etc., for $\mathfrak{N} = 1, 2, 3,$ etc.

The Hilbert space of spin-free quantum chemistry is a spin-free space. From this spin-free space we select certain subspaces, called *configuration spaces*, denoted by

$$V(\nu): \quad \mathbf{B}(\nu) = \{|\nu; i\rangle, i = 1 \text{ to } f^\nu\} \quad (2.8)$$

where

$$|\nu; i\rangle \equiv \mathbf{P}_a |\nu\rangle, \quad \mathbf{P}_a \in S_N \quad (2.9)$$

The function $|\nu\rangle$ is called a *primitive ket* and is normally taken to be an orbital product; *e.g.*

$$|\nu\rangle \equiv |\phi_1\rangle|\phi_2\rangle|\phi_3\rangle|\phi_4\rangle \dots \quad (2.10)$$

where the electron assigned to an orbital is specified by the position of the orbital in $|\nu\rangle$. The quantity

$$\nu = \phi_1^{\gamma_1} \phi_2^{\gamma_2} \phi_3^{\gamma_3} \dots \quad (2.11)$$

where $\gamma_1, \gamma_2, \gamma_3,$ etc., are the number of electrons assigned to $|\phi_1\rangle, |\phi_2\rangle, |\phi_3\rangle,$ etc., is called the *configuration* of $V(\nu)$.

A vector

$$|\nu; w\rangle \equiv \sum_i |\nu; i\rangle \langle \nu; i | w \rangle \in V(\nu) \quad (2.12)$$

Table 2.2 $K_{(\rho)}$ and $K_{(\rho)}^{[\lambda]}$ for $N = 1, 2, 3$, and 4

$[\lambda]$	$f^{[\lambda]}$						
$N = 1$		$K_{(\rho)} = \mathcal{S}$					
[1]	1	$1 \rightarrow [D]$					
$N = 2$		$K_{(\rho)} = \mathcal{S}$	(12)				
[1 ²]	1	1	-1	$\rightarrow [T]$			
[2]	1	1	1	$\rightarrow [S]$			
$N = 3$		$K_{(\rho)} = \mathcal{S}$	(12) + (13) + (23)	(123) + (132)			
[1 ³]	1	1	-3	2			$\rightarrow [Q]$
[2,1]	2	1	0	-1			$\rightarrow [D]$
[3]	1	1	3	2			(excluded)
$N = 4$		$K_{(\rho)} = \mathcal{S}$	$\Sigma(ij)$	$\Sigma(ijk)$	$\Sigma(ij)(kl)$	$\Sigma(ijkl)$	
[1 ⁴]	1	1	-6	8	3	-6	$\rightarrow [Q]$
[2,1 ²]	3	1	-2	0	-1	2	$\rightarrow [T]$
[2 ²]	2	1	0	-4	3	0	$\rightarrow [S]$
[3,1]	3	1	2	0	-1	-2	(excluded)
[4]	1	1	6	8	3	6	(excluded)

is said to be *symmetry adapted* to S_N if, and only if

$$K_{(\rho)}|\nu;w\rangle = K_{(\rho)}^{[\lambda]}|\nu;w\rangle \quad (2.13)$$

for each of the $q(N)$ class operators (Table 2.2) of S_N . [A class operator $K_{(\rho)}$ is the sum of the elements in the ρ th class. It commutes with every element in S_N . Equation 2.13 is a consequence of Schur's lemma. (ρ is a partition of N .) The set $\{K_{(\rho)}^{[\lambda]}, (\rho) \text{ ranging}\}$ of class operator eigenvalues is sufficient to assign uniquely the spin-free quantum number $[\lambda]$ (see Table 2.2). The symmetry adapted kets are $f^{[\lambda]}$ -fold degenerate with respect to the $K_{(\rho)}$ where

$$f^{[\lambda]} = \frac{N!(N-2p+1)}{p!(N-p+1)!} \quad (2.14)$$

On the basis of (2.13) we make the association

$$|\nu;w\rangle \longrightarrow |\nu;[\lambda]t\rangle \quad (2.15)$$

where $t = 1-f^{[\lambda]}$ is an arbitrary index which distinguishes among the degenerate kets.

For any pair of symmetry adapted functions from $V(\nu)$, the Wigner-Eckart theorem gives

$$\langle \nu;[\lambda]t | \mathbf{H}^{\text{SF}} | \nu;[\lambda']t' \rangle = \delta([\lambda],[\lambda'])\delta(t,t')\langle \nu;[\lambda] | \mathbf{H}^{\text{SF}} | \nu;[\lambda] \rangle \quad (2.16)$$

where $\langle \nu;[\lambda] | \mathbf{H}^{\text{SF}} | \nu;[\lambda] \rangle$, called a *reduced matrix element*, is independent of t . As a consequence of (2.16), a secular equation based on symmetry-adapted kets is factored into blocks, each block being characterized by the spin-free quantum number $[\lambda]$. An eigenket from the $[\lambda]$ th block belongs to the $[\lambda]$ th spin-free state.

Each configuration (2.11) supplies spin-free states according to the following rules.

(1) No Pauli-allowed spin-free states (*i.e.*, $[\lambda] = [2^p, 1^{N-2p}]$) are supplied by configurations for which more than two electrons are assigned to the same orbital.

(2) If q is the number of doubly occupied orbitals, then p is restricted by

$$0 \leq q \leq p \leq N/2 \quad (2.17)$$

For example, for $N = 3$ with $q = 1$, then $p = 1$ and $\mathfrak{N} = 2$ (doublet state), while with $q = 0$, then $p = 0, 1$ and $\mathfrak{N} = 4, 2$ (quartet and doublet states).

(3) The number of linearly independent kets with $[\lambda] = [2^p, 1^{N-2p}]$ and with q doubly occupied orbitals is

$$f^{q;[\lambda]} = \frac{(N-2q)!(N-2p+1)}{(p-q)!(N-q-p+1)!} \quad (2.18)$$

Methods for the construction of symmetry adapted kets are described in the Appendix.

Note that the basis

$$V(\nu): B(\nu) = \{|\nu;i\rangle, i = 1 \text{ to } f^\nu\}$$

where

$$|\nu;i\rangle = \mathbf{P}_a|\nu\rangle, \quad \mathbf{P}_a \in S_N \quad (2.19)$$

does not assign specific electrons to specific orbitals. This is the mathematical consequence of the indistinguishability of electrons. The basis kets are degenerate under a zero-order Hamiltonian

$$\mathbf{H}^0 = \sum \mathbf{H}_i \quad (2.20)$$

This degeneracy is called *exchange* or *permutation degeneracy*. The inclusion of the perturbation

$$\mathbf{H}' \equiv \sum_{i < j} \frac{e^2}{r_{ij}} \quad (2.21)$$

removes degeneracy and effects a splitting of the zero states (Figure 3.1). The splitting does not depend on spin energetics.

3. The Relative Order of Spin-Free States

We compute, in the spin-free formulation, the relative order of the several spin-free states supplied by a configuration space $V(\nu)$. We construct $V(\nu)$ from the orthonormal orbitals $|\phi_1\rangle, |\phi_2\rangle, |\phi_3\rangle$, etc., whose orbital energies $\epsilon_1 \ll \epsilon_2 \ll \epsilon_3 \dots$ are assumed to be sufficiently separated so that states from different configurations do not overlap. We treat several configurations for a system with an even number of electrons.

A. The Ground-State Configuration, $\nu = \phi_1^2, \phi_2^2, \dots, \phi_{N/2}^2$. The number of doubly occupied orbitals is $q = N/2$. By (2.17), $N/2 \leq p \leq N/2$ so $p = N/2$ and the multiplicity, $\mathfrak{N} = 1$. Thus the theory predicts that the lowest state of the system is a singlet state.

B. Excited-State Configuration, $\nu = \phi_1^2\phi_2^2 \dots \phi_i\phi_j$. The number of doubly occupied orbitals is $q = N/2 - 1$. By (2.17), $N/2 - 1 \leq p \leq N/2$, so $p = N/2 - 1$ and $N/2$ and $\mathfrak{N} = 3$ and 1. The theory predicts that an excited-state configuration $\nu = \phi_1^2\phi_2^2 \dots \phi_i\phi_j$ supplies a triplet state and a singlet state. To predict the relative order of the triplet and singlet states, we proceed as follows. We neglect doubly occupied or-

(i) He (1s2s): $V(1s2s): \{|1s\rangle|2s\rangle, |2s\rangle|1s\rangle\}$

(ii) $\det \begin{bmatrix} Q - E & K \\ K & Q - E \end{bmatrix} = 0$
 $Q = E^0 + \int (1s)^2 (e^2/r_{12}) (2s)^2 d\tau$
 $K = \int 1s2s(e^2/r_{12})1s2s d\tau > 0$

(iii) $E(1s2s;[S]) = Q + K$ $|1s2s;[S]\rangle = (|1s\rangle|2s\rangle + |2s\rangle|1s\rangle)/\sqrt{2} \rightarrow [2] \rightarrow [S]$
 $E(1s2s;[T]) = Q - K$ $|1s2s;[T]\rangle = (|1s\rangle|2s\rangle - |2s\rangle|1s\rangle)/\sqrt{2} \rightarrow [1^2] \rightarrow [T]$

(iv)
$$\frac{E^0}{\{|1s\rangle|2s\rangle, |2s\rangle|1s\rangle\}} \begin{cases} \frac{Q + K}{[2] \rightarrow [S] \rightarrow (\uparrow \downarrow)} \\ \frac{Q - K}{[1^2] \rightarrow [T] \rightarrow (\uparrow \uparrow)} \end{cases}$$

 $e^2/r_{12} = 0$ $e^2/r_{12} \neq 0$

Figure 3.1. Spin-free Hund rule: states with the lowest $[\lambda]$ multiplicity lie the lowest.

bitals and represent the configuration vector space by

$$V(\phi_i\phi_j): \{|\phi_i\rangle|\phi_j\rangle, |\phi_j\rangle|\phi_i\rangle\} \quad (3.1)$$

By analogy to the case $V(ab)$ in the Appendix

$$[\lambda] \equiv [2]; E([S]) = Q + K; |[S]\rangle = \frac{1}{\sqrt{2}}(|\phi_i\rangle|\phi_j\rangle + |\phi_j\rangle|\phi_i\rangle) \quad (3.2)$$

$$[\lambda] \equiv [1^2]; E([T]) = Q - K; |[T]\rangle = 1/\sqrt{2}(|\phi_i\rangle|\phi_j\rangle - |\phi_j\rangle|\phi_i\rangle) \quad (3.3)$$

where

$$K \equiv \langle \phi_i | \phi_j \rangle \frac{e^2}{r_{12}} |\phi_i\rangle |\phi_j\rangle \equiv \int \phi_i(2)\phi_j(1) \frac{e^2}{r_{12}} \phi_i(1)\phi_j(2) d\tau \quad (3.4)$$

Generally, $K > 0$ so the theory predicts that for the excited-state configuration, $\nu = \phi_1^2\phi_2^2 \dots \phi_i\phi_j$, the triplet state lies lower in energy than does the singlet state, and that the magnitude of the splitting is given by $2K$ (see Figure 3.1). It has been shown^{6a} that the average energy of the $[\lambda]$ th spin-free state for a vector space constructed from products of distinct degenerate orthonormal orbitals is given by

$$\bar{E}([\lambda]) = Q - \left(p^2 - p(N+1) + \frac{N(N-1)}{2} \right) \bar{K} \quad (3.5)$$

where \bar{K} is an average integral of the type defined in (3.4). By (3.5) and (2.7)

$$\bar{E}(\mathfrak{M}) = Q - \left(\frac{N^2 - 4N - 1}{4} \right) \bar{K} - \frac{\mathfrak{M}^2}{4} \bar{K} \quad (3.6)$$

(see Table 3.1). By (3.6) the theory predicts that for

Table 3.1. Average Energies of Spin-Free States

N	$[\lambda]$	p	\mathfrak{M}	$\bar{E}([\lambda])$
2	$[1^2]$	0	Triplet	$Q - K$
	$[2]$	1	Singlet	$Q + K$
3	$[1^3]$	0	Quartet	$Q - 3\bar{K}$
	$[2, 1]$	1	Doublet	Q
4	$[1^4]$	0	Quintet	$Q - 6\bar{K}$
	$[2, 1^2]$	1	Triplet	$Q - 2\bar{K}$
	$[2^2]$	2	Singlet	Q

states constructed from distinct degenerate orthonormal orbital products the average energy of the states of highest multiplicity lies the lowest. This prediction is in agreement with the empirical generalization known as *Hund's rule*, a rule which has wide but not universal application.

The multiplicity of the lowest energy state from a configuration $V = \chi^N$ (ignoring filled shells) is by (2.7), (2.17), and Hund's rule

$$\mathfrak{M}_L(\chi^N) = N - 2q_{\min} + 1 \quad (3.7)$$

where q_{\min} is the minimum number of doubly occupied orbitals in χ^N . Equation 3.7 yields a "hole theorem"

$$\mathfrak{M}_L(\chi^N) = \mathfrak{M}_L(\chi^{2\gamma-N}) \quad (3.8)$$

where γ is the number of independent orbitals of type χ , and $2\gamma - N$ is the number of holes in the χ th shell.

For a free ion, the Hamiltonian commutes with groups S_N and $[R(3)]^N$ which supply quantum numbers $[\lambda]$ (or \mathfrak{M}) and L , respectively. For atoms with unfilled shell configurations, $\nu = l^N$, the energies are expressed in terms of the Racah empirical parameters, A, B, C , etc., which represent integrals over e^2/r_{ij} . The theory predicts in most cases that the states of highest \mathfrak{M} lie the lowest. Of states of highest \mathfrak{M} , states of highest L lie the lowest. This prediction is in agreement with the empirical generalization known as *Hund's atomic rule*.

For an ion in an octahedral complex,^{6h} the Hamiltonian commutes with S_N and $[O]^N$ which supply quantum numbers $[\lambda]$ (or \mathfrak{M}) and $\alpha = A_1, A_2, E, T_1$, and T_2 , respectively. For $\nu = d^N$, the energies are expressed in terms of A, B, C , and a ligand-field parameter Δ . The energies for $\nu = d^3$ are plotted as a function of Δ/B in Figure 3.2.

There are two limiting cases: (A) the weak-field case, $\Delta/B \approx 0$, where the energies are essentially free ion energies; and (B) the strong-field case, $B/\Delta \approx 0$, where the energies are essentially the sum of the octahedral orbital energies

$$E(t^m e^n) = m(-4\Delta) + n(6\Delta) \quad (3.9)$$

The ground-state multiplicities for an N -electron ligand system in the two limiting cases are predicted by (3.7) and the following choice of orbitals.

(A) Weak-field case, $\chi^N = d^N$

$$|\chi^r\rangle = \{|dm\rangle, m = 2, 1, 0, -1, -2\}$$

Table 3.2 Ground Permutation and Spin States in the Weak-Field and Strong-Field Limits

Weak field		Strong field							
q_{min}	$[\lambda]$	S	$\mathfrak{N}\pi$						
d^1	0	[1]	$1/2$	2	t^1	0	[1]	$1/2$	2
d^2	0	[1 ²]	1	3	t^2	0	[1 ²]	1	3
d^3	0	[1 ³]	$3/2$	4	t^3	0	[1 ³]	$3/2$	4
d^4	0	[1 ⁴]	2	5	t^4	1	[2,1 ³]	1	3
d^5	0	[1 ⁵]	$5/2$	6	t^5	2	[2 ² ,1]	$1/2$	2
d^6	1	[2,1 ⁴]	2	5	t^6	3	[2 ³]	0	1
d^7	2	[2 ² ,1 ³]	$3/2$	4	t^6e^1	3	[2 ³ ,1]	$1/2$	2
d^8	3	[2 ³ ,1 ²]	1	3	t^6e^2	3	[2 ³ ,1 ²]	1	3
d^9	4	[2 ⁴ ,1]	$1/2$	2	t^6e^3	4	[2 ⁴ ,1]	$1/2$	2
d^{10}	5	[2 ⁵]	0	1	t^6e^4	5	[2 ⁵]	0	1

(B) Strong-field case, $\chi^N = t^m e^n$

$$|\chi^r\rangle = \{ |tr\rangle, r = 1, 2, 3; |er\rangle, r = 1, 2 \}$$

The predictions of the ground-state multiplicities for the weak and strong field cases are given in Table 3.2.

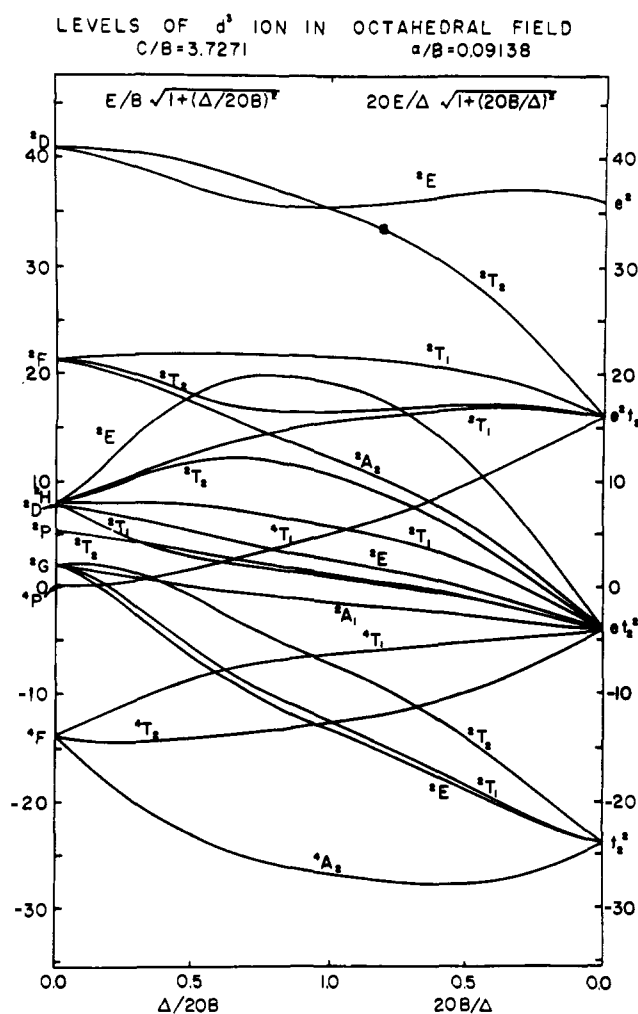


Figure 3.2

Comment. The spin-free formulation predicts the correct number of multiplicities and generally their correct order. It does this without employing spin forces, spin correlation, or Fermi holes.

4. Nonbonded Atom Repulsion

The total energy, $E(R)$, of a simple diatomic molecule can to the Born–Oppenheimer approximation be com-

puted as a function of distance to high accuracy (0.3 eV). Using the spin-free formulation, the computation employs the variation principle, a large basis set of structure functions, and exact evaluation of the

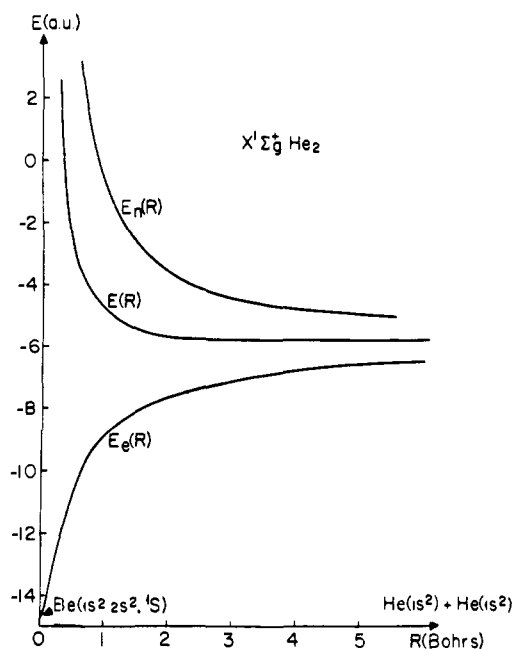


Figure 4.1

integrals. A simple example of a system exhibiting non-bonded interaction in its ground state is a system composed of two helium atoms. The results of a recent calculation³⁴ are plotted in Figure 4.1. To the Born–Oppenheimer approximation

$$E(R) = E_c(R) + \frac{4e^2}{R}$$

where $E_c(R)$ is the electronic energy and $4e^2/R$ is the nuclear repulsion. From the figure it is clear that the repulsion comes entirely from the nuclear term. The electronic energy is entirely attractive approaching the energy of $\text{Be}(1s^2 2s^2; ^1S)$ at $R = 0$.

Comment. Neither the spin energetics axiom nor the spin correlation axiom can apply since the above formulation shows that the electronic contribution is attractive and that the repulsion comes entirely from the

(34) D. J. Klein, C. E. Rodriguez, J. C. Browne, and F. A. Matsen, *J. Chem. Phys.*, 47, 4862 (1967).

repulsion between the two nuclei and not from repulsion between electrons with parallel spin.

5. The Nature of the Chemical Bond

We begin this section with a discussion of H_2 . In the molecular orbital theory one employs the configuration space

$$V(\phi_1^2): \{|\phi_1\rangle|\phi_1\rangle\} \quad (5.1)$$

Here

$$|\phi_1\rangle = \frac{1}{\sqrt{1+S}}(|a\rangle + |b\rangle) \quad (5.2)$$

where $|a\rangle$ and $|b\rangle$ are $1s$ orbitals centered on atoms A and B, respectively, and $S = \int a(i)b(i) d\tau$. Since the number of paired orbitals $q = 1$, we have by (2.17), $1 \leq p \leq 1$, so $p = 1$ ($\mathfrak{M} = 1$). Thus the molecular orbital theory predicts that the ground state of H_2 is a singlet in agreement with experiment. The molecular orbital theory predicts that the molecule does not separate into pure atomic wave functions which is not in agreement with experiment.

In the Heitler-London theory one employs the configuration space

$$V(a,b): \{ |a\rangle|b\rangle, |b\rangle|a\rangle \} \quad (5.3)$$

The number of doubly occupied orbitals is $q = 0$. By (2.17), $0 \leq p \leq 1$, so $p = 0$ ($\mathfrak{M} = 3$) and $p = 1$ ($\mathfrak{M} = 1$). Thus the configuration space supplies a triplet and a singlet. From the Appendix

$$[\lambda] = [1^2]; E([\Gamma]) = \frac{Q - \alpha}{1 - S^2}; |\Gamma\rangle = \frac{1}{\sqrt{2 - 2S^2}}(|a\rangle|b\rangle - |b\rangle|a\rangle) \quad (5.4)$$

$$[\lambda] = [2]; E([\Gamma]) = \frac{Q + \alpha}{1 + S^2}; |\Gamma\rangle = \frac{1}{\sqrt{2 + 2S^2}}(|a\rangle|b\rangle + |b\rangle|a\rangle) \quad (5.5)$$

where

$$Q \equiv \langle b|\langle a|\mathbf{H}|a\rangle|b\rangle = E^0 + \frac{1}{R} - 2 \int \frac{a(i)^2 d\tau_i}{r_{ib}} + S(ab) \quad (5.6)$$

and

$$\alpha \equiv \langle b|\langle a|\mathbf{H}|b\rangle|a\rangle = \left(E^0 + \frac{1}{R} \right) S^2 - 2S \int \frac{a(i)b(i) d\tau_i}{r_{ib}} + K(ab) \quad (5.7)$$

Now, $\alpha < 0$ for practically all values of R so the Heitler-London theory predicts that the singlet state lies lower than the triplet. Since $\alpha < 0$, Hund's rule does not apply. In contrast to the molecular orbital theory, Heitler-London theory predicts that the molecule separates into pure atomic states. Now, α decreases with increasing R for $R > 1.5 \text{ \AA}$. As a consequence, the Heitler-London theory predicts that the triplet state is unstable and the singlet state is stable against dissociation into atoms.

An analysis of the singlet state energy for H_2 into electronic and nucleonic contributions is shown in

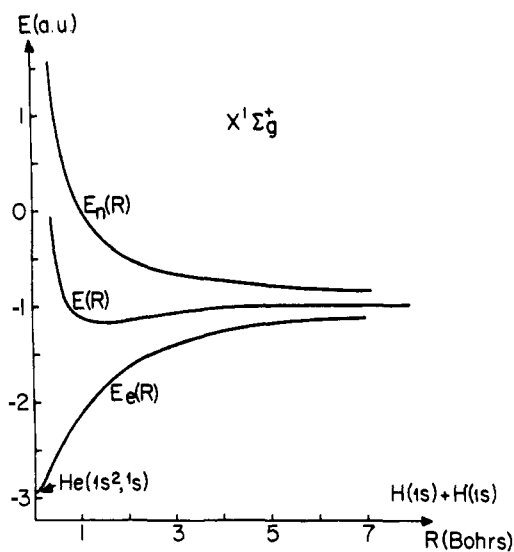


Figure 5.1

Figure 5.1. On comparison with He_2 (Figure 4.1), we note that for both systems the electronic energy is purely attractive, while the nuclear energy is purely repulsive. However, the sum of the two energies yields a minimum for H_2 , but not for He_2 . H_2 is said to be *chemically* bonded and He_2 is said to be *non-bonded*. As a consequence, H_2 in its singlet state is written $H-H$ where the line represents a chemical bond.

The Heitler-London theory is extended to polyatomic molecules^{6a,c} by invoking a configuration space

$$V(\nu): \{ |\nu; i\rangle, i = 1 \text{ to } N! \} \quad (5.8)$$

where

$$|\nu; i\rangle \equiv P_i |\nu\rangle \quad (5.9)$$

and

$$|\nu\rangle = |a\rangle|b\rangle|c\rangle \dots \quad (5.10)$$

Here the orbitals $|a\rangle, |b\rangle, |c\rangle$, etc., are atomic orbitals centered on atoms A, B, C, etc. We follow the procedure outlined in the Appendix. We first construct valence bond diagrams, D_x , in which p chemical bonds are drawn between atoms (or orbitals). For each valence bond diagram we construct a valence bond function $|\nu; x\rangle$. The valence bond function has the property that for each set of bonded atoms, say E and F (or orbitals $|e\rangle$ and $|f\rangle$)

$$(ef)|\nu; x\rangle = |\nu; x\rangle \quad (5.11)$$

where (ef) is a permutation on orbitals $|e\rangle$ and $|f\rangle$. For example, for H_2 , $D_I = A - B$, $p = 1$

$$|\nu; I\rangle = N_I(|a\rangle|b\rangle + |b\rangle|a\rangle) \text{ and } (ab)|\nu; I\rangle = |\nu; I\rangle$$

so A is bonded to B. The energy of the x th valence bond structure is given by

$$\begin{aligned} E(\nu; x) &= N_x^2 \langle \nu; x | \mathbf{H}^{\text{SF}} | \nu; x \rangle \\ &= N_x^2 \sum_i (P_i)_{xx} \langle \nu | \mathbf{H}^{\text{SF}} P_i | \nu \rangle \\ &= N_x^2 \left[Q + \sum_{\text{bonded atoms}} \langle \nu | \mathbf{H}^{\text{SF}}(ef) | \nu \rangle - \frac{1}{2} \langle \nu | \mathbf{H}^{\text{SF}}(gh) | \nu \rangle \right] \\ &\quad + \text{higher order permutations} \quad (5.12) \end{aligned}$$

If all atoms are widely separated, except for bonded

Comment. The rendering of (6.7) into spin language is

$$[2^{N/2-S}, 1^{2S}] \in [2^{N_A/2-S_A}, 1^{S_A}] \otimes [2^{N_B/2-S_B}] \quad (6.9)$$

Condition 6.9 can be simplified to

$$S = |S_A + S_B| \dots |S_A - S_B| \quad (6.10)$$

This is referred as the triangular condition, $\Delta(SS_A S_B)$. The rendering of (6.8) is

$$S_A, S_B \longrightarrow S_C, S_D \quad (6.11)$$

if, and only if, $\Delta(SS_A S_B)$ and $\Delta(SS_C S_D)$. (6.8) and (6.11) comprise the *Wigner spin conservation law*. Equation 6.10 can be derived for spin space using the properties of the group $SU(2)$ and transferring it to the spin-free space by antisymmetrization. By either derivation the rule is an expression of group theoretical restriction arising from the permutation symmetry of the spin-free Hamiltonian. The rule does not require spin space nor the quantum mechanical or classical theory of angular momentum.

7. Fine Structure

In previous sections, we have discussed the coarse structure of chemical systems. The coarse structure is completely described by a spin-free Hamiltonian, H^{SF} . Some coarse structure states display a fine structure which is not predicted by H^{SF} . To describe this fine structure we require a Hamiltonian of the form

$$H = H^{SF} \otimes \sigma + \Omega \quad (7.1)$$

which operates on a Hilbert space

$$V = V^{SF} \otimes V^S \quad (7.2)$$

a product space of spin-free and spin spaces. H^{SF} operates on V^{SF} only. Ω is an operator that contains spin-free and spin operators that operate on both V^{SF} and V^S . For systems of spherical or approximate spherical symmetry

$$\Omega \approx A^{SF} \vec{L} \cdot \vec{S} \quad (7.3)$$

where A^{SF} is a spin-free parameter. Now

$$[H, P_a^{SF}] \neq 0, P_a^{SF} \in S_N^{SF} \quad (7.4)$$

So the spin-free quantum number, $[\lambda]$, is not an exact quantum number for H . The eigenkets of H are of the form^{6f,35}

$$|\nu; \mathcal{K}\rangle = \sum_{K^{SF}} \sum_{[\lambda^{SF}]} |K^{SF}[\lambda^{SF}]\rangle \langle K^{SF}[\lambda^{SF}] | K \rangle \quad (7.5)$$

where

$$|K^{SF}[\lambda^{SF}]\rangle \equiv \sum_r^{f([\lambda^{SF}])} |K^{SF}[\lambda^{SF}]r\rangle \otimes |M[\lambda^{SF}]r\rangle \quad (7.6)$$

is an antisymmetric ket; that is, it changes sign under $\mathbf{P}^{tot} = \mathbf{P}^{SF} \otimes \mathbf{P}^S$; $|K^{SF}[\lambda^{SF}]r\rangle$ is a symmetry-adapted spin-free ket and $|M[\lambda^{SF}]r\rangle$ is a symmetry-adapted spin ket. $[\lambda^{SF}]$ and $[\lambda^{SF}]$ are conjugate partitions. \mathcal{K} is a quantum number which has the following meaning.

(i) For systems with spherical symmetry, *i.e.*, atoms, $\mathcal{K} = \{J, K\}$ where $J = |L + S| \dots |L - S|$ is the total angular momentum quantum number and K identifies states with the same J according to the sequence in energy.

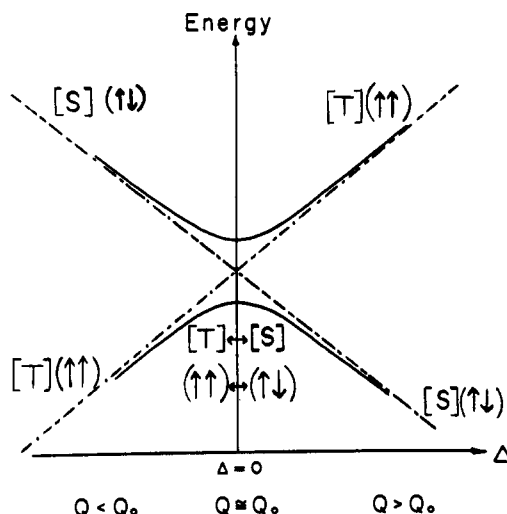


Figure 7.1

(ii) For systems with point group symmetry, *e.g.*, transition metal complexes, $\mathcal{K} = \{\alpha, K\}$ where α identifies the irreducible representation of the double point group and K identifies states with the same α according to the sequence in energy.

(iii) For systems with no symmetry, $\mathcal{K} = \{K\}$ where K identifies the states according to the sequence in energy.

These quantum numbers are employed to identify the fine structure components. According to (7.5), the eigenket $|\mathcal{K}\rangle$ contains (*i.e.*, mixes) kets with different K^{SF} and $[\lambda^{SF}]$. As the system moves adiabatically over an energy surface, the per cent $[\lambda^{SF}]$ character in $|\mathcal{K}\rangle$ changes and $[\lambda^{SF}]$ is not conserved. Only the \mathcal{K} quantum number is conserved.

As an example we consider a vector space spanned by two kets of the form (7.6) which we designate by $|[S]\rangle$ and $|[T]\rangle$. The energies, $E^0[S]$ and $E^0[T]$, of these kets under the spin-free Hamiltonian are taken to be functions of some internal coordinate Q and are degenerate at $Q = Q^0$ (see Figure 7.1). The eigenvalues and eigenkets of the Hamiltonian in (7.1) are as follows.

$$K = \text{II}$$

$$E(\text{II}) = (E^0[S] + E^0[T] + Y)/2$$

$$|[S][T]; \text{II}\rangle = \frac{1}{\sqrt{1+a^2}}(a|[T]\rangle - |[S]\rangle)$$

$$K = \text{I}$$

$$E(\text{I}) = (E^0[S] + E^0[T] - Y)/2$$

$$|[S][T]; \text{I}\rangle = \frac{1}{\sqrt{1+a^2}}(|[T]\rangle + a|[S]\rangle)$$

$$Y = \sqrt{\Delta^2 + 4\langle\Omega\rangle^2}$$

$$a = \frac{2\langle\Omega\rangle}{\Delta - Y}$$

$$\Delta = E^0[T] - E^0[S]$$

$$\langle\Omega\rangle = \langle [T] | \Omega | [S] \rangle$$

For $Q \ll Q_0$, $\Delta \ll 0$, $a \cong 0$, $E(\text{I}) \cong E[T]$, $|[S][T]; \text{I}\rangle \cong |[T]\rangle$, and the system is almost a pure triplet. For $Q \gg Q_0$, $\Delta \gg 0$, $a \rightarrow \infty$, $E(\text{I}) \cong E[S]$, $|[S][T]; \text{I}\rangle \cong |[S]\rangle$, and the system is almost a pure singlet. At intermedi-

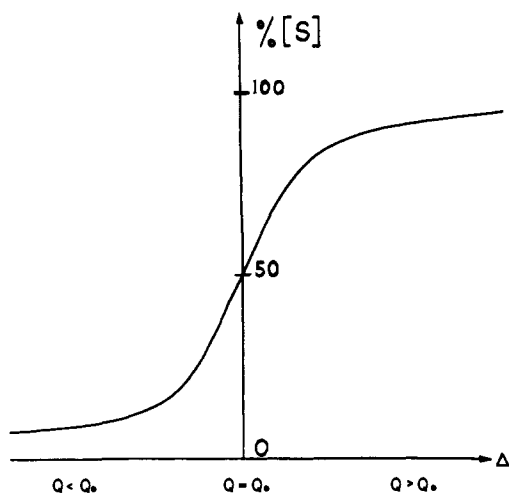
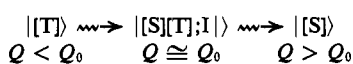


Figure 7.2

ate Q the triplet and singlet states are strongly mixed. The per cent of $|[S]\rangle$ in $|[S][T];I\rangle$ is given by

$$\%[S] = \frac{a^2}{1 + a^2} 100$$

The quantity is plotted in Figure 7.2 and shows a smooth continuous transition from "pure" triplet to "pure" singlet. Because it is a transition from a "pure" triplet system to a "pure" singlet system, the transition is sometimes called an *intersystem crossover*. Because it is an adiabatic transition it does not involve the emission or absorption of radiation; it is called a *radiationless transition*. The process can be diagrammed as follows.



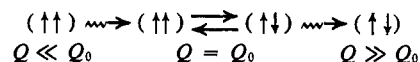
For $|Q - Q_0| \gg 0$, the surface is accurately described by a spin-free Hamiltonian, $[\lambda]$ (and S) is a good quantum number, and spin does not play a major role. It is only in the region $Q = Q_0$ that spin energetics become important. For $Q = Q_0$, the coarse structure given by H^{SF} yields a doubly degenerate state. The inclusion of Ω splits the coarse structure into two fine structure components labeled II and I, respectively. The magnitude of the splitting (e.g., $E(\text{II}) - E(\text{I})$) is determined by the form of Ω .

Comments. The spin language rendering of (7.4) is

$$[H, S^2] \neq 0$$

so S is not an exact quantum number to H . We see that S is a good quantum number if, and only if, the spin-free quantum number $[\lambda]$ is a good quantum number.

An intersystem crossover in the spin up (\uparrow)-spin down (\downarrow) representation is described as follows. Since the spin vector can point only up or down, the transition triplet ($\uparrow\uparrow$) \rightsquigarrow singlet ($\uparrow\downarrow$), requires that an electron do a spin-flip at a precise instant in time or at a precise value of Q . There is no evidence that such an abrupt spin-flip occurs. The misconception occurs because it is believed that spin and spin arrows provide an adequate labeling of the states for the entire process. The spin-flip problem can be circumvented by the following representation



The symbol $(\uparrow\uparrow) \rightleftharpoons (\uparrow\downarrow)$ represents a resonance hybrid of the state characterized by $(\uparrow\uparrow)$ and that characterized by $(\uparrow\downarrow)$. The $\%(\uparrow\downarrow)$ in the hybrid changes with Q as shown in Figure 7.2.

We see that the prohibition against the intersystem crossover based on a principle of spin conservation is invalid. Indeed there is evidence that in most molecules (e.g., benzene, methylene, chromium complexes) the rate of intersystem crossover is high enough to compete with radiative and chemical processes.

8. Hyperfine Structure^{6c}

To predict hyperfine structure, we require a Hamiltonian of the form

$$H = H^{SF} \otimes \sigma \otimes \sigma + \Omega \quad (8.1)$$

which operates on a Hilbert space

$$V = V^{SF} \otimes V^S \otimes V^T \quad (8.2)$$

where V^T is the nuclear spin space and Ω contains electronic and nuclear spin operators. For this system $[\lambda^{SF}]$, while not an exact quantum number, is nevertheless usually a very good one. We take for the isotropic interaction operator in the K th spin-free state at the a th nucleus the effective hyperfine Hamiltonian

$$\Omega(a) = A_K^{SF}(a) \vec{S} \cdot \vec{I} \quad (8.3)$$

where

$$A_K^{SF}(a) = \frac{\pi\beta\gamma_0\hbar}{2S} \hat{\rho}_K(a) \quad (8.4)$$

Here $\hat{\rho}_K(a)$ is the unpaired electron density, a spin-free quantity which can be computed from spin-free wave functions. The unpaired electron density at point \vec{r} for the K th electronic state with $[\lambda^{SF}] = [2^p, 1^{N-2p}]$ is given by

$$\hat{\rho}_K(\vec{r}) = \sum_{i=1}^N \rho_{K^i}(\vec{r}) - 2 \sum_{i=1}^p \rho_{K^{2i}}(\vec{r}) \quad (8.5)$$

where $\rho_{K^i}(\vec{r})$ is the electron density for the K th state contributed to point \vec{r} by the i th electron. Note that the number of unpaired electrons is

$$v = \int \hat{\rho}_K(\vec{r}) d\vec{r} = N - 2p \quad (8.6)$$

where v is the *valence*. For $[\lambda] = [2^{N/2}]$ (singlet state)

$$\hat{\rho}_K(\vec{r}) = 0 \quad (8.7)$$

We give below several examples of unpaired electron densities. For simplicity we have assumed that the orbitals are orthonormal. Example I: He(1s2s;³S)

$$\hat{\rho}_K(\vec{r}) = |1s(\vec{r})|^2 + |2s(\vec{r})|^2$$

Example II: Li(1s²2s;²S)

$$\hat{\rho}_K(\vec{r}) = |2s(\vec{r})|^2$$

Example III: allyl radical C₃H₅(*abc*;²A₁)

$$\hat{\rho}_K(\vec{r}) = \frac{2}{3}|a(\vec{r})|^2 - \frac{1}{3}|b(\vec{r})|^2 + \frac{2}{3}|c(\vec{r})|^2$$

The unpaired electron density at the a th nucleus can be evaluated from the experimentally determined

hyperfine interaction constants $A_K(a)$. The $\beta_K(a)$ which are determined from experiment agree well with those computed from the high quality spin-free eigenfunctions of a spin-free Hamiltonian. If a poor quality wave function is used, the agreement with experiment may be poor. An example is Li(1s²2s;²S) for which the experimental value of $\beta_K(a) = 0.2313(a_0^{-3})$. If a nodeless Slater function is used for the 2s orbital, the computed value is zero.

Comment. It is often implied that an unpaired electron can spin polarize the spins of paired electrons. For example, the incorrect result for Li(1s²2s) mentioned above has been attributed to the neglect of spin polarization of the 1s²(↑↓) shell by 2s(↑) electrons. The effect of spin polarization is too small to be detectable by current techniques.

9. Paramagnetic Susceptibility

The order of the coarse structure states is determined by the spin-free Hamiltonian. If the ground state

$$[\lambda_g] = [2^{p_g}, 1^{N-2p_g}] \quad (9.1)$$

is widely separated from the excited states, the paramagnetic susceptibility is given by

$$\chi = N \frac{4\beta^2 S_g(S_g + 1)}{3kT} \quad (9.2)$$

where

$$S_g = N/2 - p_g$$

In this case the magnetic susceptibility is determined by spin-free energetics.

10. Conclusion

We have exhibited a spin-free theory of the coarse structure of chemistry. It is a complete theory, and there exists no experimental evidence against it. Spin is shown to be either a theoretically irrelevant quantum number or a poor one. The conventional spin formulation of the spin-free theory is no more than an alternative formulation of the coarse structure problem and has the weakness that it suggests to many chemists that spin plays an energy determining role in coarse structure chemistry.

Appendix

We present two methods for the construction of kets symmetry adapted to S_N .

A. The Secular Equation Method. A corollary of the Wigner-Eckart theorem (2.16) is that eigenfunctions of \mathbf{H}^{SF} in a configuration vector space $V(\nu)$ are symmetry adapted with respect to S_N . The procedure, using this corollary, is as follows.

(1) Select a configuration vector space

$$V(\nu): \{|\nu; i\rangle, i = 1 \text{ to } f^r\} \quad (A1)$$

where

$$|\nu; i\rangle \equiv \mathbf{P}_a |\nu\rangle, \mathbf{P}_a \in S_N \quad (A2)$$

(2) Construct and solve the secular equation for \mathbf{H}^{SF} on $V(\nu)$

$$\det[\langle \nu; i | \mathbf{H}^{\text{SF}} | \nu; j \rangle - \lambda \langle \nu; i | \nu; j \rangle] = 0 \quad (A3)$$

The matrix elements in (A3) are related as follows

$$\langle \nu; i | \mathbf{H}^{\text{SF}} | \nu; j \rangle = \langle \nu | \mathbf{P}_a^{-1} \mathbf{H}^{\text{SF}} \mathbf{P}_b | \nu \rangle = \langle \nu | \mathbf{H}^{\text{SF}} \mathbf{P}_c | \nu \rangle \quad (A4)$$

where

$$\mathbf{P}_c = \mathbf{P}_a^{-1} \mathbf{P}_b \quad (A5)$$

Denote eigenvalues and eigenfunctions by $E(\nu; K)$ and $|\nu; Kk\rangle$ where $K = A, B, C$, etc., is the energy sequence and k distinguishes among kets with the same eigenvalue.

(3) Assign quantum numbers.

- Assign $[\lambda]$ by means of (2.13) and Table 2.2.
- Exclude functions with $[\lambda] \neq [2^p, 1^{N-2p}]$.
- Compute multiplicity by (2.7). Label kets $[\lambda] = [S], [D], [T]$, etc., for $\mathfrak{M} = 1, 2, 3$, etc.
- Assign additional quantum numbers for other commuting groups.
 - For $R(3)$

$$\mathbf{L}^2 |\nu; [\lambda] t\rangle = L(L + 1) |\nu; [\lambda] t\rangle \quad (A6)$$

where $\mathbf{L}^2 = (\sum_{i=1}^N \vec{\mathbf{L}}_i)^2$ is the Casimir operator for $[R(3)]^N$, the N th rank inner direct product of $R(3)$. The states are labeled S, P, D, etc., for $L = 0, 1, 2$, etc.

(ii) Finite point group symmetry, G

$$\mathbf{K}_{(\rho)} |\nu; [\lambda] t\rangle = K_{(\rho)}^\alpha |\nu; [\lambda] t\rangle \quad (A7)$$

where $\mathbf{K}_{(\rho)}$ is the class operator for $[G]^N$, the N th rank inner direct product of G . For $G = O_h$ (the octahedral group), $\alpha = A_1, A_2, E, T_1$, and T_2 (the g and u are suppressed). There follow examples for $N = 1, 2, 3$. We ignore point group symmetry. We employ the following definitions for matrix elements

$$Q \equiv \langle \nu | \mathbf{H}^{\text{SF}} \mathcal{Q} | \nu \rangle$$

$$\alpha \equiv \langle \nu | \mathbf{H}^{\text{SF}}(12) | \nu \rangle$$

$$\beta \equiv \langle \nu | \mathbf{H}^{\text{SF}}(13) | \nu \rangle$$

$$\gamma \equiv \langle \nu | \mathbf{H}^{\text{SF}}(23) | \nu \rangle$$

$$\delta \equiv \langle \nu | \mathbf{H}^{\text{SF}}(123) | \nu \rangle = \langle \nu | \mathbf{H}^{\text{SF}}(132) | \nu \rangle = 0$$

for orthogonal orbitals

$N = 1; \nu = a$

$$(1) V(\nu): \{|a\rangle\}$$

$$(2) \det[Q - \lambda] = 0$$

$$E(\nu; A) = Q \quad |\nu; A\rangle = |a\rangle$$

$$(3) |\nu; A\rangle \equiv |\nu; [1]\rangle \equiv |\nu; [D]\rangle$$

$N = 2; \nu = ab$

$$(1) V(\nu): \{|a\rangle|b\rangle, |b\rangle|a\rangle\}$$

$$(2) \det \begin{pmatrix} Q - \lambda & \alpha \\ \alpha & Q - \lambda \end{pmatrix} = 0$$

$$E(\nu; B) = Q + \alpha \quad |\nu; B\rangle = 1/\sqrt{2}(|a\rangle|b\rangle + |b\rangle|a\rangle)$$

$$E(\nu; A) = Q - \alpha \quad |\nu; A\rangle = 1/\sqrt{2}(|a\rangle|b\rangle - |b\rangle|a\rangle)$$

$$(3) |\nu; B\rangle \equiv |\nu; [2]\rangle \equiv |\nu; [S]\rangle$$

$$|\nu; A\rangle \equiv |\nu; [1^2]\rangle \equiv |\nu; [T]\rangle$$

$N = 2; \nu = a^2$

$$(1) V(\nu): \{|a\rangle|a\rangle\}$$

$$(2) \det[Q - \lambda] = 0$$

$$E(\nu; \mathbf{A}) = Q \quad |\nu; \mathbf{A}\rangle = |a\rangle|a\rangle$$

$$(3) |\nu; \mathbf{A}\rangle = |\nu; [2]\rangle \equiv |\nu; [\mathbf{S}]\rangle$$

$$N = 3; \nu = abc$$

$$(1) V(\nu): \{ |a\rangle|b\rangle|c\rangle, |b\rangle|a\rangle|c\rangle, |c\rangle|b\rangle|a\rangle, |a\rangle|c\rangle|b\rangle, \\ |c\rangle|a\rangle|b\rangle, |b\rangle|c\rangle|a\rangle \}$$

$$(2) \det \begin{bmatrix} Q - \lambda & \alpha & \beta & \gamma & 0 & 0 \\ \alpha & Q - \lambda & 0 & 0 & \gamma & \beta \\ \beta & 0 & Q - \lambda & 0 & \alpha & \gamma \\ \gamma & 0 & 0 & Q - \lambda & \beta & \alpha \\ 0 & \gamma & \alpha & \beta & Q - \lambda & \delta \\ 0 & \beta & \gamma & \alpha & \delta & Q - \lambda \end{bmatrix} = 0$$

$$E(\nu; \mathbf{D}) = Q + \alpha + \beta + \gamma$$

$$|\nu; \mathbf{D}\rangle = 1/\sqrt{6}(|a\rangle|b\rangle|c\rangle + |b\rangle|a\rangle|c\rangle + |a\rangle|c\rangle|b\rangle \\ |c\rangle|b\rangle|a\rangle + |c\rangle|a\rangle|b\rangle + |b\rangle|c\rangle|a\rangle)$$

$$E(\nu; \mathbf{C}) = Q + \Gamma \quad (\text{occurs twice})$$

$$|\nu; \mathbf{C}1\rangle = \frac{1}{\sqrt{3 + 3F^2}}(|a\rangle|b\rangle|c\rangle + |b\rangle|a\rangle|c\rangle - \\ \frac{(\sqrt{3}F + 1)}{2}|c\rangle|b\rangle|a\rangle + \frac{(\sqrt{3}F + 1)}{2}|a\rangle|c\rangle|b\rangle + \\ \frac{(\sqrt{3}F - 1)}{2}|c\rangle|a\rangle|b\rangle - \frac{(\sqrt{3}F + 1)}{2}|b\rangle|c\rangle|a\rangle)$$

$$|\nu; \mathbf{C}2\rangle = \frac{1}{\sqrt{3 + 3F^2}}(F|a\rangle|b\rangle|c\rangle - F|b\rangle|a\rangle|c\rangle + \\ \frac{(F - \sqrt{3})}{2}|b\rangle|b\rangle|a\rangle + \frac{(F + \sqrt{3})}{2}|a\rangle|c\rangle|b\rangle - \\ \frac{(F + \sqrt{3})}{2}|c\rangle|a\rangle|b\rangle + \frac{(\sqrt{3} - F)}{2}|b\rangle|c\rangle|a\rangle)$$

$$E(\nu; \mathbf{B}) = Q - \Gamma \quad (\text{occurs twice})$$

$$|\nu; \mathbf{B}1\rangle = \frac{1}{\sqrt{3 + 3F^2}}(F|a\rangle|b\rangle|c\rangle + F|b\rangle|a\rangle|c\rangle + \\ \frac{(\sqrt{3} - F)}{2}|c\rangle|b\rangle|a\rangle - \frac{(\sqrt{3} + F)}{2}|a\rangle|c\rangle|b\rangle - \\ \frac{(\sqrt{3} + F)}{2}|c\rangle|a\rangle|b\rangle - \frac{(\sqrt{3} - F)}{2}|b\rangle|c\rangle|a\rangle)$$

$$|\nu; \mathbf{B}2\rangle = \frac{1}{\sqrt{3 + 3F^2}}(-|a\rangle|b\rangle|c\rangle + |b\rangle|a\rangle|c\rangle - \\ \frac{(\sqrt{3}F + 1)}{2}|c\rangle|b\rangle|a\rangle + \frac{(\sqrt{3}F - 1)}{2}|a\rangle|c\rangle|b\rangle + \\ \frac{(1 - \sqrt{3}F)}{2}|c\rangle|a\rangle|b\rangle + \frac{(\sqrt{3}F + 1)}{2}|b\rangle|c\rangle|a\rangle)$$

$$E(\nu; \mathbf{A}) = Q - \alpha - \beta - \gamma$$

$$|\nu; \mathbf{A}\rangle = 1/\sqrt{6}(|a\rangle|b\rangle|c\rangle - |b\rangle|a\rangle|c\rangle - |c\rangle|b\rangle|a\rangle + \\ |a\rangle|c\rangle|b\rangle + |c\rangle|a\rangle|b\rangle + |b\rangle|a\rangle|c\rangle)$$

$$\Gamma = \sqrt{(\alpha - \beta)^2 + (\alpha - \gamma)^2 + (\beta - \gamma)^2}/\sqrt{2}$$

$$F = \frac{2}{\sqrt{3}} \frac{\Gamma - \alpha + \beta/2 + \gamma/2}{(\beta - \gamma)}$$

$$(3) |\nu; \mathbf{D}1\rangle = |\nu; [3]\rangle \text{ excluded}$$

$$|\nu; \mathbf{C}r\rangle = |\nu; \mathbf{B}[2,1]r\rangle = |\nu; \mathbf{B}[\mathbf{D}]r\rangle, r = 1, 2$$

$$|\nu; \mathbf{B}r\rangle = |\nu; \mathbf{A}[2,1]r\rangle = |\nu; \mathbf{A}[\mathbf{D}]r\rangle, r = 1, 2$$

$$|\nu; \mathbf{A}1\rangle = |\nu; [1^3]\rangle = |\nu; [Q]\rangle$$

$$N = 3; \nu = a^2b$$

$$(1) V(\nu) = \{ |a\rangle|a\rangle|b\rangle, |a\rangle|b\rangle|a\rangle, |b\rangle|a\rangle|a\rangle \}$$

$$(2) \det \begin{bmatrix} Q - \lambda & \alpha & \alpha \\ \alpha & Q - \lambda & \alpha \\ \alpha & \alpha & Q - \lambda \end{bmatrix} = 0$$

$$E(\nu; \mathbf{B}) = Q + 2\alpha$$

$$|\nu; \mathbf{B}\rangle = 1/\sqrt{3}(|a\rangle|a\rangle|b\rangle + |a\rangle|b\rangle|a\rangle + |b\rangle|a\rangle|a\rangle)$$

$$E(\nu; \mathbf{A}) = Q - \alpha \quad (\text{occurs twice})$$

$$|\nu; \mathbf{B}1\rangle = 1/\sqrt{6}(2|a\rangle|a\rangle|b\rangle - |a\rangle|b\rangle|a\rangle - |b\rangle|a\rangle|a\rangle)$$

$$|\nu; \mathbf{B}2\rangle = 1/\sqrt{2}(|a\rangle|b\rangle|a\rangle - |b\rangle|a\rangle|a\rangle)$$

$$(3) |\nu; \mathbf{B}r\rangle = |\nu; [2,1]r\rangle = |\nu; [\mathbf{D}]r\rangle, r = 1, 2$$

$$|\nu; \mathbf{B}\rangle = |\nu; [3]\rangle \text{ excluded}$$

$$N = 3; \nu = a^3$$

$$(1) V(\nu) = \{ |a\rangle|a\rangle|a\rangle \}$$

$$(2) \det[Q - \lambda] = 0$$

$$E(\nu; \mathbf{A}) = Q$$

$$|\nu; \mathbf{A}\rangle = |a\rangle|a\rangle|a\rangle$$

$$(3) |\nu; \mathbf{A}\rangle = |\nu; [3]\rangle \text{ excluded}$$

B. The Structure Operator Method. For an orbital product primitive function $|\nu\rangle$ with no more than $q \leq p$ doubly occupied orbitals and a spin-free quantum number $[\lambda] = [2^p, 1^{N-2p}]$ we proceed as follows.

(1) Draw structure diagrams, D_x , by tying orbitals together in pairs with p arrows. Identical orbitals must be tied.

(2) Construct a structure function $|\nu; \kappa\rangle$ for D_x by means of the structure operator κ . Thus

$$|\nu; \kappa\rangle = \kappa|\nu\rangle/\sqrt{C}$$

where

$$C = 2^p p!(N - p)!$$

An arrow reversal in D_x changes the sign of κ and $|\nu; \kappa\rangle$. A structure function is invariant under the transposition of paired orbitals. If $|a\rangle$ and $|b\rangle$ are paired

$$P(ab)|\nu; \kappa\rangle = |\nu; \kappa\rangle$$

It follows from (2.18) that a structure function can be expressed as a sum of $f^{q;[\lambda]}$ linearly independent structure functions. Thus

$$|\nu; \kappa\rangle = \sum_{\kappa'} f^{q;[\lambda]} |\nu; \kappa'\rangle \langle \kappa' | \kappa \rangle$$

A structure function can be simultaneously symmetry adapted to other groups; e.g., $[R(3)]^N$ or $[G]^N$.

For the $[\lambda]$ th state and the primitive ket $|\nu\rangle$, we employ the vector space

$$V(\nu; [\lambda]): \{ |\nu; \kappa\rangle, \kappa = 1 \text{ to } f^{q;[\lambda]} \}$$

The basis set may be any set of $f^{a;[\lambda]}$ linearly independent structure functions. The representation of \mathbf{H}^{SF} in this basis is given by

$$\langle \nu; \kappa | \mathbf{H}^{\text{SF}} | \nu; \kappa' \rangle = \sum (\mathbf{P}_a)_{\kappa \kappa'} \langle \nu | \mathbf{H}^{\text{SF}} \mathbf{P}_a | \nu \rangle$$

The number $(\mathbf{P}_a)_{\kappa \kappa'}$, called the *Pauling number*, can be computed by several schemes. The eigenvalues and eigenfunctions are denoted

$$E(\nu; [\lambda] K): |\nu; [\lambda] K\rangle = \sum_{\kappa} f^{a; [\lambda]} |\nu; \kappa\rangle \langle \nu; \kappa | K \rangle$$

We construct an integer structure diagram for D_x for the spin-free state $[\lambda] = [2^p, 1^{N-2p}]$ by connecting by arrows the members of each of p pairs of N integers. We denote by D_I the integer structure diagram obtained by pairing integer 1 with integer 2, integer 3 with integer 4, etc. The structure operator for D_x is defined by

$$\kappa \equiv \epsilon(P_{I_x}) N_I M_I P_{I_x}$$

Here P_{I_x} is the permutation that converts D_x into D_I and $\epsilon(P_{I_x}) = \pm 1$ for P_{I_x} , an even or odd permutation.

M_I for D_I is the sum of all the permutations that permute the paired integers, and N_I is the antisymmetric sum of the permutation of the unpaired integers

$$M_I = \vartheta + (12) + (34) + \dots + (12)(34) \dots$$

$$N_I = \vartheta - (23) - (24) \dots + (13)(24) - (15) \dots$$

Only $f^{[\lambda]}$ of the structure operators are linearly independent. The structure function for the integer structure diagram D_x and the primitive ket $|\nu\rangle$ is given by

$$|\nu; \kappa\rangle = \kappa |\nu\rangle / \sqrt{C}$$

where $C \equiv 2^p p! (N - p)!$. We convert the integer structure diagrams into an orbital structure diagram with respect to primitive ket $|\nu\rangle$ by replacing the integers by the orbitals assigned to them in $|\nu\rangle$.

$$N = 1 \quad |\nu\rangle = |a\rangle$$

$$[\lambda] = [1], f^{[\lambda]} = 1$$

$$(1) \quad D_I = 1 = a$$

$$(2) \quad \kappa_I = \vartheta$$

$$(3) \quad |\nu; I\rangle = |a\rangle$$

$$N = 2 \quad |\nu\rangle = |a\rangle|b\rangle$$

$$[\lambda] = [1^2], \mathfrak{N} = 3, f^{[\lambda]} = 1$$

$$(1) \quad D_I = 1 \ 2 = a \ b$$

$$(2) \quad \kappa_I = \vartheta - (12)$$

$$(3) \quad |\nu; I\rangle = 1/\sqrt{2}(|a\rangle|b\rangle - |b\rangle|a\rangle)$$

$$[\lambda] = [2], \mathfrak{N} = 1, f^{[\lambda]} = 1$$

$$(1) \quad D_I = 1 \rightarrow 2 = a \rightarrow b$$

$$(2) \quad \kappa_I = \vartheta + (12)$$

$$(3) \quad |\nu; I\rangle = 1/\sqrt{2}(|a\rangle|b\rangle + |b\rangle|a\rangle)$$

$$N = 3 \quad |\nu\rangle = |a\rangle|b\rangle|c\rangle$$

$$[\lambda] = [1^3], \mathfrak{N} = 4, f^{[\lambda]} = 1$$

$$(1) \quad D_I = 1 \ 2 \ 3 = a \ b \ c$$

$$(2) \quad \kappa_I = \vartheta - (12) - (13) - (23) + (123) + (132)$$

$$(3) \quad |\nu; I\rangle = 1/\sqrt{6}(|a\rangle|b\rangle|c\rangle - |b\rangle|a\rangle|c\rangle - |c\rangle|b\rangle|a\rangle - |a\rangle|c\rangle|b\rangle + |c\rangle|a\rangle|b\rangle + |b\rangle|c\rangle|a\rangle)$$

$$[\lambda] = [2, 1], \mathfrak{N} = 2, f^{[\lambda]} = 2$$

$$(1) \quad D_I \equiv 1 \rightarrow 2 = a \rightarrow b$$

$$D_{II} \equiv 1 \quad \begin{array}{ccc} & 3 & c \\ & \uparrow & \uparrow \\ & 3 & c \end{array} \quad P_{I \ II} = (13)$$

$$D_{III} \equiv 1 \quad \begin{array}{ccc} & 3 & c \\ & \searrow & \swarrow \\ & 3 & c \end{array} \quad P_{I \ III} = (23)$$

$$(2) \quad \kappa_I = (\vartheta - (13))(\vartheta + (12)) = \vartheta + (12) - (13) - (123)$$

$$\kappa_{II} = (-1)\kappa_I(13) = \vartheta - (13) + (23) - (132)$$

$$\kappa_{III} = (-1)\kappa_I(23) = (12) - (23) - (123) + (132)$$

$$\kappa_{III} = \kappa_I - \kappa_{II}$$

$$(3) \quad |\nu; I\rangle = 1/2(|a\rangle|b\rangle|c\rangle + |b\rangle|a\rangle|c\rangle - |c\rangle|b\rangle|a\rangle - |b\rangle|c\rangle|a\rangle)$$

$$|\nu; II\rangle = -1/2(|a\rangle|b\rangle|c\rangle - |c\rangle|b\rangle|a\rangle - |a\rangle|c\rangle|b\rangle - |c\rangle|a\rangle|b\rangle)$$

$$|\nu; III\rangle = 1/2(|b\rangle|a\rangle|c\rangle - |a\rangle|c\rangle|b\rangle + |c\rangle|a\rangle|b\rangle - |b\rangle|c\rangle|a\rangle)$$

$$|\nu; III\rangle = |\nu; I\rangle - |\nu; II\rangle$$

For $|\nu\rangle = |a\rangle|b\rangle|c\rangle$ and $[\lambda] = [2, 1]$

$$V(\nu; [2, 1]): \{|\nu; I\rangle, |\nu; II\rangle\}$$

The secular equation for $V(\nu; [2, 1])$

$$\det \begin{bmatrix} Q + \alpha - \gamma/2 - & Q/2 + \beta - \alpha/2 - \\ \beta/2 - \lambda & \gamma/2 - \lambda/2 \\ -Q/2 + \beta - \alpha/2 - & Q + \gamma - \alpha/2 - \\ \gamma/2 - \lambda/2 & \beta/2 - \lambda \end{bmatrix}$$

$$E(\nu; B[2, 1]) = Q + \Gamma; |\nu; B[2, 1]\rangle = (|\nu; I\rangle + A|\nu; II\rangle)/(1 + A + A^2)^{1/2}$$

$$E(\nu; A[2, 1]) = Q - \Gamma; |\nu; A[2, 1]\rangle = (|\nu; I\rangle + B|\nu; II\rangle)/(1 - B + B^2)^{1/2}$$

$$A = \frac{\alpha - \gamma/2 - \beta/2 - \Gamma}{\beta - \alpha/2 - \gamma/2 + 1/2\Gamma}$$

and

$$B = \frac{\alpha - \gamma/2 - \beta/2 + \Gamma}{\beta - \alpha/2 - \gamma/2 - 1/2\Gamma}$$

The allyl radical $|\nu\rangle = |\pi_a\rangle|\pi_b\rangle|\pi_c\rangle$

$$\gamma = \alpha, \Gamma = \alpha - \beta, A = 1, \text{ and } B = -1$$

$$E(\nu; B[2, 1]) = Q + \alpha - \beta; |\nu; B[2, 1]\rangle = 1/\sqrt{3}(|\nu; I\rangle + |\nu; II\rangle)$$

$$E(\nu; A[2, 1]) = Q - \alpha + \beta; |\nu; B[2, 1]\rangle = (|\nu; I\rangle - |\nu; II\rangle) = |\nu; III\rangle$$

Note that the A state is a pure valence bond state. The A state is the ground state for the allyl radical. $|\nu; A[2, 1]\rangle$ was employed for the unpaired spin density calculation in section 8.